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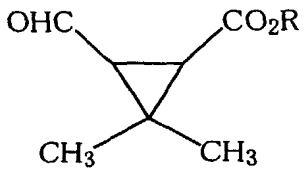
(54) Title: PROCESS FOR THE PRODUCTION OF TRANS-3,3-DIMETHYL-2-FORMLCYCLOPROPANE CARBOXYLIC ACID ESTERS



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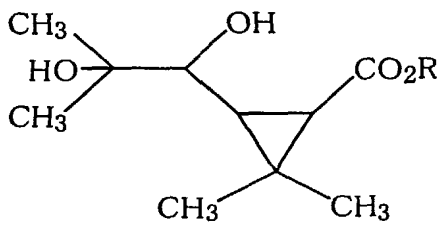

(1)

(57) Abstract: A process for the production of an aldehyde of formula (2): wherein R is substituted or unsubstituted alkyl, substituted or unsubstituted aryl, or substituted or unsubstituted aralkyl, which process includes reacting a diol compound of formula (1): wherein R is as defined above, with an oxidizing agent selected from a periodic acid compound, a hypohalogenous acid compound, a bismuth compound, or an activated manganese dioxide.

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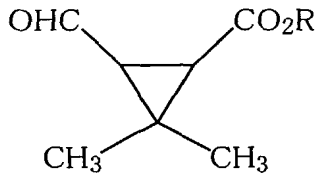
PROCESS FOR THE PRODUCTION OF TRANS-3,3-DIMETHYL-2-FORMYLCYCLOPROPANE CARBOXYLIC ACID ESTERS

Technical Field

The present invention relates to a process for the production of an aldehyde.

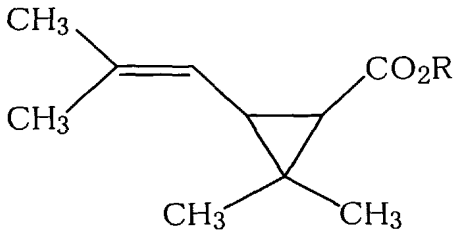
Background Art

The aldehyde of formula (2):



(2)

wherein R is substituted or unsubstituted alkyl, substituted or unsubstituted aryl, substituted or unsubstituted aralkyl, are very important compounds as the intermediates for the synthesis of pyrethroid-type household agents for epidemic prevention, pesticides, or the like (see, *e.g.*, JP-B 46-24695). For example, there have been known a process in which olefin compounds of formula (4):



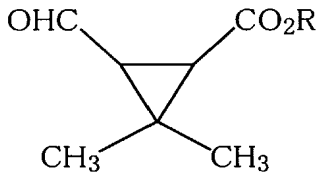
(4)

wherein R is as defined above, are oxidized in the presence of an osmium tetroxide catalyst (see, *e.g.*, J. Labelled Compounds and Radiopharmaceuticals,

13, 561 (1977)) and a process in which the olefin compounds of the above formula (4) are ozone-oxidized (see, *e.g.*, JP-B 46-24695). However, osmium tetroxide is highly toxic, and the ozone oxidation method requires special equipment taking into account fire prevention; therefore, both cannot be said to be a fully satisfactory production process from an industrial point of view.

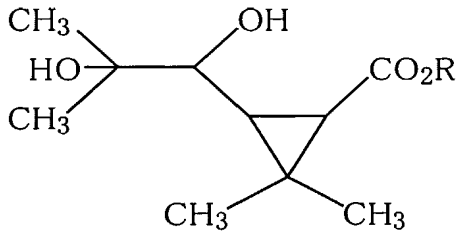
Disclosure of Invention

Under these circumstances, the present inventors have intensively studied to develop a process for producing the aldehyde of formula (2):



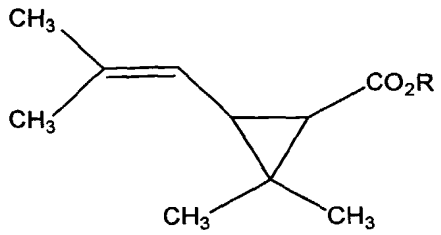
(2)

wherein R is substituted or unsaturated alkyl, substituted or unsaturated aryl, or substituted or unsaturated aralkyl, in an industrially more advantageous manner, and have found the aldehyde of formula (2) can be obtained by reacting a diol compound of formula (1):



(1)

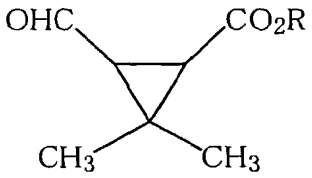
wherein R is as defined above, with oxidizing agents such as sodium periodate, which diol compound of formula (1) can easily be derived from the olefin compound of formula (4):



(4)

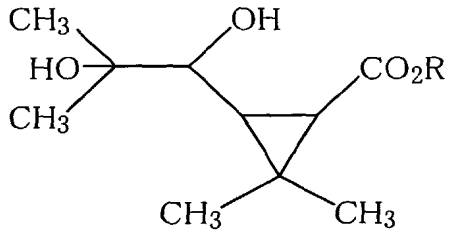
wherein R is as defined above, without using highly toxic reagents or special equipment, thereby completing the present invention.

Thus the present invention provides a process for the production of an aldehyde of formula (2):



(2)

wherein R is substituted or unsaturated alkyl, substituted or unsaturated aryl, or substituted or unsaturated aralkyl, which process comprises reacting a diol compound of formula (1):

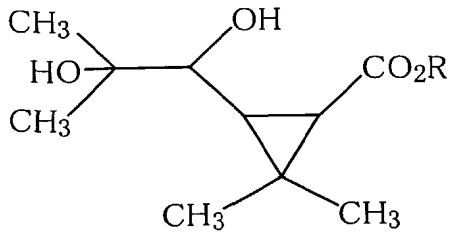


(1)

wherein R is as defined above, with an oxidizing agent selected from a periodic acid compound, a hypohalogenous acid compound, a bismuth compound, or an activated manganese dioxide.

Mode for Carrying Out the Invention

First, the following will describe the diol compound of formula (1):



(1)

(hereinafter abbreviated as diol (1))

wherein R is substituted or unsaturated alkyl, substituted or unsaturated aryl, or substituted or unsaturated aralkyl.

In the formula of the diol (1), R represents substituted or unsaturated alkyl, substituted or unsaturated aryl, or substituted or unsaturated aralkyl.

The substituted or unsaturated alkyl may include straight or branched chain, or cyclic alkyl groups of 1 to 20 carbon atoms, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-heptadecyl, n-octadecyl, n-nonadecyl, n-icosyl, cyclopropyl, 2,2-dimethylcyclopropyl, cyclopentyl, cyclohexyl, and menthyl, and alkyl groups substituted with alkoxy (*e.g.*, C_1-C_4 alkoxy) such as methoxy, ethoxy, n-propoxy, or tert-butoxy; aryloxy (*e.g.*, phenoxy or naphthyloxy), aralkyloxy (*e.g.*, phenylalkyloxy such as benzyloxy or naphthylalkyloxy such as naphthylmethoxy), and halogen such as fluorine, chlorine, and bromine. The alkyl groups substituted with such substituents may include chloromethyl, fluoromethyl, trifluoromethyl, methoxymethyl, ethoxymethyl, and 2-methoxyethyl.

The substituted or unsubstituted aryl may include phenyl and naph-

thyl groups, and phenyl and naphthyl groups substituted with a substituent(s), such as the above-mentioned substituted or unsubstituted alkyl, aryl (*e.g.*, phenyl or naphthyl), above-mentioned alkoxy, aralkyl (*e.g.*, phenylalkyl such as benzyl or naphthylalkyl such as naphthylmethyl), the above-mentioned aryloxy, the above-mentioned aralkyloxy, and the above-mentioned halogen. Specific examples of the substituted phenyl and naphthyl groups include, for example, 2-methylphenyl, 4-chlorophenyl, 4-methylphenyl, 4-methoxyphenyl, and 3-phenoxyphenyl.

The substituted or unsubstituted aralkyl may include those which are composed of the above-mentioned substituted or unsubstituted aryl group and the above-mentioned substituted or unsubstituted alkyl group, such as benzyl, 4-chlorobenzyl, 4-methylbenzyl, 4-methoxybenzyl, 3-phenoxybenzyl, 2,3,5,6-tetrafluorobenzyl, 2,3,5,6-tetrafluoro-4-methylbenzyl, 2,3,5,6-tetrafluoro-4-methoxybenzyl, and 2,3,5,6-tetrafluoro-4-methoxymethylbenzyl.

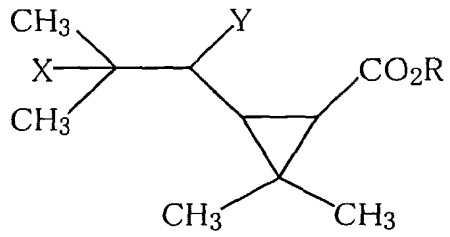
Preferred is the unsubstituted alkyl.

The diol (1) may include methyl 3,3-dimethyl-2-(2-methyl-1,2-dihydroxypropyl)cyclopropanecarboxylate, ethyl 3,3-dimethyl-2-(2-methyl-1,2-dihydroxypropyl)cyclopropanecarboxylate, isopropyl 3,3-dimethyl-2-(2-methyl-1,2-dihydroxypropyl)cyclopropanecarboxylate, tert-butyl 3,3-dimethyl-2-(2-methyl-1,2-dihydroxypropyl)cyclopropanecarboxylate, cyclohexyl 3,3-dimethyl-2-(2-methyl-1,2-dihydroxypropyl)cyclopropanecarboxylate, menthyl 3,3-dimethyl-2-(2-methyl-1,2-dihydroxypropyl)cyclopropanecarboxylate, benzyl 3,3-dimethyl-2-(2-methyl-1,2-dihydroxypropyl)cyclopropanecarboxylate, 4-chlorobenzyl 3,3-dimethyl-2-(2-methyl-1,2-dihydroxypropyl)cyclopropanecarboxylate, 2,3,5,6-tetrafluorobenzyl 3,3-dimethyl-2-(2-methyl-1,2-dihydroxypropyl)cyclopropanecarboxylate, 2,3,5,6-tetrafluoro-4-methylbenzyl 3,3-dimethyl-2-(2-methyl-1,2-dihydroxypropyl)cyclopropanecarboxylate,

2,3,5,6-tetrafluoro-4-methoxybenzyl 3,3-dimethyl-2-(2-methyl-1,2-dihydroxypropyl)cyclopropanecarboxylate, 2,3,5,6-tetrafluoro-4-methoxymethylbenzyl 3,3-dimethyl-2-(2-methyl-1,2-dihydroxypropyl)cyclopropanecarboxylate, and 3-phenoxybenzyl 3,3-dimethyl-2-(2-methyl-1,2-dihydroxypropyl)cyclopropanecarboxylate.

The diol (1) may exist in cis-form where the group of $-CO_2R$ and the 2-methyl-1,2-dihydroxypropyl group are present on the same side, relative to the cyclopropane ring plane, or in trans-form where these groups are present on the opposite sides, and either any one of them or a mixture of them may be used in the present invention. Further, the diol (1) contains asymmetric carbon atoms in the molecule and has optical isomers, and either individuals or mixtures of the optical isomers may be used in the present invention.

The diol (1) can be obtained, for example, by reacting a hydroperoxy compound of formula (3):



(3)

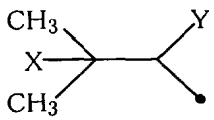
(hereinafter abbreviated as hydroperoxy compound (3))

wherein R is as defined above; and one of X and Y is hydroxyl and the other is hydroperoxy, with the reducing agent as described below.

The hydroperoxy compound (3) may include methyl 3,3-dimethyl-2-(2-methyl-2-hydroperoxy-1-hydroxypropyl)cyclopropanecarboxylate, ethyl 3,3-dimethyl-2-(2-methyl-2-hydroperoxy-1-hydroxypropyl)cyclopropanecarboxylate, isopropyl 3,3-dimethyl-2-(2-methyl-2-hydroperoxy-1-hydroxypropyl)cyclopropanecarboxylate, tert-butyl 3,3-dimethyl-2-(2-methyl-2-hydro-

peroxy-1-hydroxypropyl)cyclopropanecarboxylate, cyclohexyl 3,3-dimethyl-2-(2-methyl-2-hydroperoxy-1-hydroxypropyl)cyclopropanecarboxylate, menthyl 3,3-dimethyl-2-(2-methyl-2-hydroperoxy-1-hydroxypropyl)cyclopropanecarboxylate, benzyl 3,3-dimethyl-2-(2-methyl-2-hydroperoxy-1-hydroxypropyl)-cyclopropanecarboxylate, 4-chlorobenzyl 3,3-dimethyl-2-(2-methyl-2-hydroperoxy-1-hydroxypropyl)cyclopropanecarboxylate, 2,3,5,6-tetrafluorobenzyl 3,3-dimethyl-2-(2-methyl-2-hydroperoxy-1-hydroxypropyl)cyclopropanecarboxylate, 2,3,5,6-tetrafluoro-4-methylbenzyl 3,3-dimethyl-2-(2-methyl-2-hydroperoxy-1-hydroxypropyl)cyclopropanecarboxylate, 2,3,5,6-tetrafluoro-4-methoxybenzyl 3,3-dimethyl-2-(2-methyl-2-hydroperoxy-1-hydroxypropyl)-cyclopropanecarboxylate, 2,3,5,6-tetrafluoro-4-methoxymethylbenzyl 3,3-dimethyl-2-(2-methyl-2-hydroperoxy-1-hydroxypropyl)cyclopropanecarboxylate, 3-phenoxybenzyl 3,3-dimethyl-2-(2-methyl-2-hydroperoxy-1-hydroxypropyl)cyclopropanecarboxylate, methyl 3,3-dimethyl-2-(2-methyl-2-hydroxy-1-hydroperoxypropyl)cyclopropanecarboxylate, ethyl 3,3-dimethyl-2-(2-methyl-2-hydroxy-1-hydroperoxypropyl)cyclopropanecarboxylate, isopropyl 3,3-dimethyl-2-(2-methyl-2-hydroxy-1-hydroperoxypropyl)cyclopropanecarboxylate, and tert-butyl 3,3-dimethyl-2-(2-methyl-2-hydroxy-1-hydroperoxypropyl)cyclopropanecarboxylate.

The hydroperoxy compound (3) may exist in cis-form where the group of $-CO_2R$ and the group of the following formula:



are present on the same side, relative to the cyclopropane ring plane, or in trans-form where these groups are present on the opposite sides, and either any one of them or a mixture of them may be used in the present invention.

Further, the hydroperoxy compound (3) contains asymmetric carbon atoms in the molecule and has optical isomers, and either individuals or mixtures of the optical isomers may be used in the present invention.

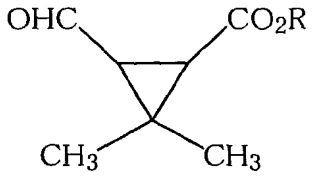
The reducing agent may include an inorganic reducing agent such as sodium thiosulfate, sodium borohydride, and sodium hydrosulfide; organic reducing agents such as dimethyl sulfide, diethyl sulfide, thiodiglycol, 2-mercaptoethanol, 2-(ethylthio)ethanol, and triphenylphosphine; and hydrogen/palladium catalyst, with the organic reducing agent being preferred. The amount of reducing agent that may be suitably used is usually 1 mole, per mol of the hydroperoxy compound (3), and there is no particular upper limit thereof. Since too great amounts are disadvantageous from an economical point of view, the amount of reducing agent that may be suitably used is usually not more than 5 moles, per mol of the hydroperoxy compound (3).

The reaction conditions such as reaction temperatures and reaction solvents in the reaction of the hydroperoxy compound (3) with a reducing agent may be suitably selected depending on the kind of reducing agent.

After completion of the reaction, for example, the reaction mixture may be subjected to concentration or column chromatography to isolate the diol (1) from the reaction mixture, and the isolated diol (1) may be used in the reaction with an oxidizing agent as described below. Alternatively, if necessary, water and/or a water-immiscible organic solvent may be added to the reaction mixture, followed by extraction, and the resulting organic layer containing the diol (1) may be used as such, or after concentration, in the reaction with an oxidizing agent as described below. The reaction mixture obtained may also be used as such in the reaction with an oxidizing agent as described below. Of course, the isolated diol (1) may be purified by ordinary means of purification, such as distillation and column chromatography, before use in the reaction with an oxidizing agent as described below.

When the hydroperoxy compound (3) in trans-form is used, the diol in trans-form is obtained. When the hydroperoxy compound in cis-form is used, the diol in cis-form is obtained. When the optically active hydroperoxy compound is used, the optically active diol is obtained.

The following will describe a process for producing the aldehyde of formula (2):



(2)

(hereinafter abbreviated as aldehyde (2))

wherein R is as defined above, by oxidizing the diol (1).

For example, when the diol (1) obtained by reacting the above-mentioned hydroperoxy compound (3) with a reducing agent is used, the diol (1) may be isolated from the reaction mixture obtained in the above reaction, or the reaction mixture may also be used as such. When the reducing agent remains in the reaction mixture, it is necessary to use an oxidizing agent in an sufficient amount to oxidize the remaining reducing agent. Therefore, it is preferred from an economical point of view that the diol (1) is separated or isolated from the reaction mixture for use in the present step or the reaction mixture is used after removal of the remaining reducing agent.

The oxidizing agent may include a periodic acid compound, a hypohalogenous acid compound, a bismuth compound, and activated manganese dioxide. The periodic acid compound may include periodic acid and periodic acid alkali metal salts such as sodium periodate and potassium periodate. The hypohalogenous acid compound may include hypohalogenous acid; hypohalogenous acid alkaline earth metal salts such as calcium hypochlorite;

and hypohalogenous acid alkali metal salts such as sodium hypochlorite. The bismuth compound may include pentavalent bismuth compounds such as triphenylbismuth carbonate, triphenyldichlorobismuth, μ-oxobis(chlorotriphenylbismuth), and sodium bismuthate. The activated manganese dioxide can be obtained according to the known method in which manganese sulfate is reacted with potassium permanganate.

The amount of oxidizing agent that may be suitably used is usually 1 to 5 moles, preferably 1 to 3 moles, per mol of the diol (1). As described above, when the diol (1) obtained by reacting the hydroperoxy compound (3) with a reducing agent are used, the reaction mixture containing the diol (1) is used as such, and the reducing agent that may remain in the reaction mixture is usually oxidized with a sufficient amount of oxidizing agent. The oxidizing agent may be used as such, or for example, as an aqueous solution.

The reaction of the diol (1) with the oxidizing agent is usually carried out by contacting and mixing both of them.

The reaction temperature is usually −10 to 100°C. The present reaction is usually carried out in a solvent which dissolves the diol (1). The solvent may include water; alcohol solvents such as methanol, ethanol, and tert-butyl alcohol; nitrile solvents such as acetonitrile and propionitrile; ether solvents such as diethyl ether, methyl tert-butyl ether, and tetrahydrofuran; ester solvents such as ethyl acetate; aromatic hydrocarbon solvents such as toluene and xylene; and halogenated hydrocarbon solvents such as dichloromethane, dichloroethane, chloroform, carbon tetrachloride, chlorobenzene, and dichlorobenzene. The amounts for their use are not particularly limited. These solvents may be used alone or in combination.

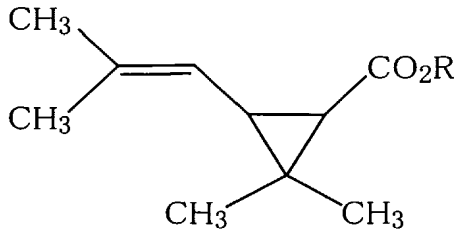
After completion of the reaction, for example, the reaction mixture is subjected as such, or if necessary, after removal of insoluble matter by filtration, to concentration and/or column chromatography, if necessary, to

isolate the aldehyde (2) from the reaction mixture. Alternatively, if necessary, water and/or the above-mentioned water-immiscible organic solvent is added to the reaction mixture, followed by extraction, and the resulting organic layer is subjected to concentration to isolate the aldehyde (2). The isolated aldehyde (2) can be purified by means such as distillation and/or column chromatography.

The aldehyde (2) thus obtained may include methyl 3,3-dimethyl-2-formylcyclopropanecarboxylate, ethyl 3,3-dimethyl-2-formylcyclopropanecarboxylate, isopropyl 3,3-dimethyl-2-formylcyclopropanecarboxylate, tert-butyl 3,3-dimethyl-2-formylcyclopropanecarboxylate, cyclohexyl 3,3-dimethyl-2-formylcyclopropanecarboxylate, menthyl 3,3-dimethyl-2-formylcyclopropanecarboxylate, benzyl 3,3-dimethyl-2-formylcyclopropanecarboxylate, 4-chlorobenzyl 3,3-dimethyl-2-formylcyclopropanecarboxylate, 2,3,5,6-tetrafluorobenzyl 3,3-dimethyl-2-formylcyclopropanecarboxylate, 2,3,5,6-tetrafluoro-4-methylbenzyl 3,3-dimethyl-2-formylcyclopropanecarboxylate, 2,3,5,6-tetrafluoro-4-methoxybenzyl 3,3-dimethyl-2-formylcyclopropanecarboxylate, 2,3,5,6-tetrafluoro-4-methoxymethylbenzyl 3,3-dimethyl-2-formylcyclopropanecarboxylate, and 3-phenoxybenzyl 3,3-dimethyl-2-formylcyclopropanecarboxylate.

When the diol (1) in trans-form is used, the aldehyde (2) in trans-form is obtained. When the diol (1) in cis-form is used, the aldehyde (2) in cis-form is obtained. When the optically active diol (1) is used, the optically active aldehyde (2) is obtained.

The hydroperoxy compound (3) can be obtained, for example, by reacting an olefin compound of formula (4):



(4)

(hereinafter abbreviated as olefin (4))

wherein R is as defined above, with hydrogen peroxide in the presence of a metal oxide catalyst obtained by reacting at least one selected from the group consisting of tungsten metal, molybdenum metal; tungsten compounds comprising tungsten and an element of Group IIIb, IVb, Vb, or VIb; and molybdenum compounds comprising molybdenum and an element of Group IIIb, IVb, Vb, or VIb, with hydrogen peroxide.

The olefin (4) may include methyl 3,3-dimethyl-2-(2-methyl-1-propenyl)cyclopropanecarboxylate, ethyl 3,3-dimethyl-2-(2-methyl-1-propenyl)-cyclopropanecarboxylate, isopropyl 3,3-dimethyl-2-(2-methyl-1-propenyl)-cyclopropanecarboxylate, tert-butyl 3,3-dimethyl-2-(2-methyl-1-propenyl)-cyclopropanecarboxylate, cyclohexyl 3,3-dimethyl-2-(2-methyl-1-propenyl)-cyclopropanecarboxylate, menthyl 3,3-dimethyl-2-(2-methyl-1-propenyl)-cyclopropanecarboxylate, benzyl 3,3-dimethyl-2-(2-methyl-1-propenyl)cyclopropanecarboxylate, 4-chlorobenzyl 3,3-dimethyl-2-(2-methyl-1-propenyl)-cyclopropanecarboxylate, 2,3,5,6-tetrafluorobenzyl 3,3-dimethyl-2-(2-methyl-1-propenyl)cyclopropanecarboxylate, 2,3,5,6-tetrafluoro-4-methylbenzyl 3,3-dimethyl-2-(2-methyl-1-propenyl)cyclopropanecarboxylate, 2,3,5,6-tetrafluoro-4-methoxybenzyl 3,3-dimethyl-2-(2-methyl-1-propenyl)cyclopropanecarboxylate, 2,3,5,6-tetrafluoro-4-methoxymethylbenzyl 3,3-dimethyl-2-(2-methyl-1-propenyl)cyclopropanecarboxylate, and 3-phenoxybenzyl 3,3-dimethyl-2-(2-methyl-1-propenyl)cyclopropanecarboxylate.

The olefin (4) may exist in cis-form where the group of $-CO_2R$ and the

2-methyl-1-propenyl group are present on the same side, relative to the cyclopropane ring plane, or in trans-form where these groups are present on the opposite sides, and either any one of them or a mixture of them may be used in the present invention. Further, the olefin (4) contains asymmetric carbon atoms in the molecule and has optical isomers, and either individuals or mixtures of the optical isomers may be used in the present invention.

The catalyst used in the reaction of olefin (4) with hydrogen peroxide is a metal oxide catalyst obtained by reacting at least one (hereinafter abbreviated the metal compound(s)) selected from the group consisting of tungsten metal, molybdenum metal; a tungsten compound comprising tungsten and an element of Group IIIb, IVb, Vb, or VIb; and a molybdenum compound comprising molybdenum and an element of Group IIIb, IVb, Vb, or VIb, with hydrogen peroxide. The tungsten compound comprising tungsten and an element of Group IIIb may include tungsten boride. The tungsten compound comprising tungsten and an element of Group IVb may include tungsten carbide and tungsten silicide. The tungsten compound comprising tungsten and an element of Group Vb may include tungsten nitride and tungsten phosphide. The tungsten compound comprising tungsten and an element of Group VIb may include tungsten oxide, tungstic acid, sodium tungstate, and tungsten sulfide.

The molybdenum compound comprising molybdenum and an element of Group IIIb may include molybdenum boride. The molybdenum compound comprising molybdenum and an element of Group IVb may include molybdenum carbide and molybdenum silicide. The molybdenum compound comprising molybdenum and an element of Group Vb may include molybdenum nitride and molybdenum phosphide. The molybdenum compound comprising molybdenum and an element of Group VIb may include molybdenum oxide, molybdic acid, and molybdenum sulfide.

In these metal compounds, tungsten metal, molybdenum metal, tungsten boride, molybdenum boride, tungsten sulfide, and molybdenum sulfide are preferred. These metal compounds may be used alone or in combination. The use of a metal compound of a fine particle is preferred in that it makes easier the preparation of a metal compound catalyst as a catalyst.

The hydrogen peroxide to be reacted with such metal or metal compound is usually used as an aqueous solution, but it may also be used as an organic solvent solution. From the viewpoint of easy handling, the use of an aqueous hydrogen peroxide solution is preferred. The concentration of hydrogen peroxide in an aqueous solution or an organic solvent solution of hydrogen peroxide is not particularly limited, but taking into account volume efficiency and safety, it is usually 1 to 60 wt.%. The aqueous hydrogen peroxide solution may usually be used as such a commercially available product, or if necessary, after concentration adjustment by dilution or concentration. The organic solvent solution of hydrogen peroxide can be prepared, for example, by means such as extraction of an aqueous hydrogen peroxide solution with an organic solvent, or distillation in the presence of an organic solvent.

The reaction of the metal or metal compound with hydrogen peroxide is usually carried out in an aqueous solution. Of course, it may be carried out in an organic solvent such as an ether solvent (*e.g.*, diethyl ether, methyl tert-butyl ether, tetrahydrofuran), an ester solvent (*e.g.*, ethyl acetate), an alcohol solvent (*e.g.*, methanol, ethanol, tert-butanol), or a nitrile solvent (*e.g.*, acetonitrile, propionitrile), or in a mixed solvent of such an organic solvent and water.

The amount of hydrogen peroxide that may be used in the preparation of the metal oxide catalyst is usually not less than 3 moles, preferably

not less than 5 moles, per mol of the metal or metal compound, and there is no particular limit thereof.

The reaction of the metal or metal compound with hydrogen peroxide is usually carried out by mixing both of them, and to improve the contact efficiency of the metal or metal compound and hydrogen peroxide, the reaction is preferably carried out while stirring so that the metal or metal compound can sufficiently disperse in the solution for the preparation of the metal oxide catalyst. From the viewpoints of an increase in the contact efficiency of the metal or metal compound and hydrogen peroxide and easier control in the preparation of the metal oxide catalyst, it is preferred to use the metal or metal compound with a fine particle diameter, such as a powdered metal or metal compound. The temperature in the preparation of the metal oxide catalyst is usually −10°C to 100°C.

The reaction of the metal or the metal compound with hydrogen peroxide in water or in an organic solvent makes all or some of the metal or metal compound dissolved, so that a uniform solution or suspension containing the metal oxide catalyst can be prepared. The metal oxide catalyst may be isolated from the solution for the preparation, for example, by concentration, and used as a catalyst, or the solution for the preparation may be used as a catalyst solution without treatment.

The reaction of olefin (4) with hydrogen peroxide in the presence of the metal oxide catalyst thus obtained gives hydroperoxy compound (3). The amount of metal oxide catalyst used as a catalyst is usually not less than 0.001 mole, per mol of the olefin (4), and there is no particular upper limit thereof. From an economical point of view, the amount of metal oxide catalyst used is not more than 1 mole, per mol of the olefin (4).

The hydrogen peroxide is usually used as an aqueous solution. Of course, an organic solvent solution of hydrogen peroxide may be used. The

concentration of hydrogen peroxide in an aqueous solution or an organic solvent solution of hydrogen peroxide is not particularly limited, but taking into account volume efficiency and safety, it is usually 1 to 60 wt.%. The aqueous hydrogen peroxide solution may usually be used as such a commercially available product, or if necessary, after concentration adjustment by dilution or concentration. The organic solvent solution of hydrogen peroxide can be prepared, for example, by means such as extraction of an aqueous hydrogen peroxide solution with an organic solvent, or distillation in the presence of an organic solvent.

The amount of hydrogen peroxide used is usually not less than 1 mole, per mol of the olefin (4), and there is no particular upper limit thereof. From an economical point of view, the amount of hydrogen peroxide used is usually not more than 10 moles, per mol of the olefin (4). When the solution for the preparation of the metal oxide catalyst, which is obtained by reacting the metal compound with hydrogen peroxide, is used as a catalyst, the amount of hydrogen peroxide used may be set in addition to the amount of hydrogen peroxide contained in the solution for the preparation.

The reaction of the olefin (4) with hydrogen peroxide is usually carried out in an aqueous solvent or in an organic solvent. The organic solvent may include ether solvents such as diethyl ether, methyl tert-butyl ether, and tetrahydrofuran; ester solvents such as ethyl acetate; alcohol solvents such as methanol, ethanol, and tert-butanol; and nitrile solvents such as acetonitrile and propionitrile. The amount of aqueous or organic solvent used is not particularly limited, but taking into account volume efficiency, it is not more than 100 parts by weight, per 1 part by weight of the olefin (4).

The reaction of olefin (4) with hydrogen peroxide gives the hydroperoxy compound (3), but in addition to the hydroperoxy compound (3), for example, the products as the further oxidized hydroperoxy compound (3) are

also formed as minor by-products. Lower water content in the reaction system has a tendency to selectively provide the hydroperoxy compound (3), and therefore, it is preferred that the reaction is carried out under the conditions that the water content in the reaction system is low. The method for carrying out the reaction under low water content conditions may include coexistence with a desiccant in the reaction system. The desiccant may include anhydrous magnesium sulfate, anhydrous sodium sulfate, anhydrous boric acid, and polyphosphoric acid.

Too high reaction temperature increases the formation of the further oxidized hydroperoxy compound (3) as by-products, and therefore, for selectively obtaining the hydroperoxy compound (3), it is preferred that the reaction is carried out in the range of 0°C to 65°C, while monitoring the conversion of the olefin (4).

The reaction of olefin (4) with hydrogen peroxide is usually carried out under normal pressure conditions, but it may also be carried out under pressurized conditions

After completion of the reaction, for example, 90% or more of the olefin (4) is converted, the reaction mixture is subjected, for example, to extraction, phase separation and/or concentration, and column chromatography, if necessary, so that the hydroperoxy compound (3) can be isolated from the reaction mixture. Alternatively, if necessary, water and/or a water-immiscible organic solvent is added to the reaction mixture, followed by extraction, and the resulting organic layer is subjected to concentration, so that the hydroperoxy compound (3) can also isolated. The isolated hydroperoxy compound (3) can be purified by ordinary means of purification, such as distillation.

The water-immiscible organic solvent may include aromatic hydrocarbon solvents such as toluene and xylene; halogenated hydrocarbon sol-

vents such as dichloromethane, chloroform, and chlorobenzene; ether solvents such as diethyl ether, methyl tert-butyl ether, and tetrahydrofuran; and ester solvents such as ethyl acetate. The amount for their use are not particularly limited.

When the olefin (4) in trans-form is used, the hydroperoxy compound (3) in trans-form is obtained. When the olefin (4) in cis-form is used, the hydroperoxy compound (3) in cis-form is obtained. When the optically active olefin (4) is used, the optically active hydroperoxy compounds (3) is obtained.

Examples

The present invention will hereinafter be further illustrated by the following Examples; however, the present invention is not limited to these Examples. The analysis was carried out by gas chromatography (hereinafter abbreviated as GC) and high-pressure liquid chromatography (hereinafter abbreviated as LC).

Example 1

A 100-mL flask equipped with a stirrer was charged with 2.2 g of methyl trans-3,3-dimethyl-2-(1,2-dihydroxy-2-methylpropyl)cyclopropanecarboxylate (content: 97 wt.%) and 30 mL of toluene. To this was added dropwise 16 g of 15 wt.% aqueous sodium periodate solution at an internal temperature of 5°C to 10°C over 20 minutes. After stirring at the same temperature to effect reaction, insoluble matter in the reaction mixture was removed by filtration. The insoluble matter was washed with toluene, and the washing solution was mixed with the filtrate previously obtained. The filtrate after mixing was left at rest, followed by phase separation. The aqueous layer was extracted with toluene. The resulting toluene layer was mixed with the organic layer obtained by the previous phase separation to

give 64.6 g of the organic layer containing methyl trans-3,3-dimethyl-2-formylcyclopropanecarboxylate. Content: 2.3 wt.%. Yield: 97%.

Example 2

A 50-mL four-neck flask equipped with a stirrer and a reflux condenser was charged with 0.4 g of methyl trans-3,3-dimethyl-2-(1,2-dihydroxy-2-methylpropyl)cyclopropanecarboxylate and 10 mL of dichloromethane. To the solution obtained was added 1 g of triphenylbismuth carbonate at room temperature, followed by stirring at the same temperature for 2 hours to effect reaction. After the internal temperature was increased to 40°C, stirring was continued for 1 hour to effect reaction. Then, insoluble matter in the reaction mixture was removed by filtration. The LC analysis of the resulting filtrate showed that methyl trans-3,3-dimethyl-2-formylcyclopropanecarboxylate (the remaining starting material was observed). LC corrected percentage area: 53%.

Example 3

A 20-mL flask equipped with a stirrer was charged with 0.4 g of methyl trans-3,3-dimethyl-2-(1,2-dihydroxy-2-methylpropyl)cyclopropanecarboxylate and 2.6 g of acetonitrile. To the resulting solution were added dropwise 4.9 g of a mixed solution containing 2.4 g of calcium hypochlorite, 25 mL of water, and 2.5 mL of glacial acetic acid at room temperature. After stirring at room temperature for 15 hours to effect reaction, the LC analysis showed methyl trans-3,3-dimethyl-2-formylcyclopropanecarboxylate was produced (the remaining starting material was hardly observed). LC corrected percentage area: 51%.

Example 4

A 100-mL four-neck flask equipped with a stirrer was charged with 1 g of methyl trans-3,3-dimethyl-2-(1,2-dihydroxy-2-methylpropyl)cyclopropanecarboxyalte and 50 mL of dichloromethane, and then charged with 2 g of

activated manganese dioxide at room temperature, followed by stirring for 2 days to effect reaction. The result of analysis showed that methyl trans-3,3-dimethyl-2-formylcyclopropanecarboxylate was produced (the inversion rate of the starting material was 60%). Yield: 55%.

Example 5

To 167 g of a toluene solution containing methyl trans-3,3-dimethyl-2-(1-hydroxy-2-hydroperoxy-2-methylpropyl)cyclopropanecarboxylate and methyl trans-3,3-dimethyl-2-(2-hydroxy-1-hydroperoxy-2-methylpropyl)-cyclopropanecarboxylate (the content for methyl trans-3,3-dimethyl-2-(1-hydroxy-2-hydroperoxy-2-methylpropyl)cyclopropanecarboxylate and methyl trans-3,3-dimethyl-2-(2-hydroxy-1-hydroperoxy-2-methylpropyl)cyclopropanecarboxylate: 74% (the value of LC corrected percentage area)) was added 8 g of dimethyl sulfide, followed by stirring at room temperature for 2 days to effect reaction, giving a reaction mixture containing methyl trans-3,3-dimethyl-2-(1,2-dihydroxy-2-methylpropyl)cyclopropanecarboxylate.

The reaction mixture was concentrated under reduced pressure conditions to give about 90 g of concentrated residue. To the concentrated residue was added 40 g of toluene and then added dropwise 70 g of 15 wt.% aqueous sodium periodate solution at an internal temperature of 0°C over 10 minutes. After stirring at the same temperature for 1 hour and holding to effect reaction, insoluble matter was removed by filtration. The resulting filtrate was subjected to phase separation to give 140 g of the organic layer containing methyl trans-3,3-dimethyl-2-formylcyclopropanecarboxylate. The content for methyl trans-3,3-dimethyl-2-formylcyclopropanecarboxylate: 5 wt.%.

Example 6

A 300-mL flask equipped with a stirrer and a reflux condenser was charged with 15 g of water and 2 g of tungsten metal powder, to which 7.4 g

of 60 wt.% aqueous hydrogen peroxide solution was added dropwise at an internal temperature of 40°C while stirring over 20 minutes, followed by stirring at the same temperature for 1 hour to effect reaction, giving a uniform solution. To the solution was added 1.4 g of boric acid, and the mixture was stirred at an internal temperature of 40°C for 1 hour and held, followed by cooling to room temperature and addition of 76 g of tert-butyl alcohol and 2 g of 60 wt.% aqueous hydrogen peroxide solution. Then, 26.6 g of anhydrous magnesium sulfate was added over 20 minutes, followed by stirring at room temperature for another 2 hours. To the slurry solution obtained were added dropwise simultaneously a mixed solution containing 20 g of methyl trans-3,3-dimethyl-2-(2-methyl-1-propenyl)cyclopropanecarboxylate and 24 g of tert-butyl alcohol, and 10 g of 60 wt.% aqueous hydrogen peroxide solution over 4 hours, followed by stirring at an internal temperature of 5°C for 39 hours to effect reaction. Then, 120 g of water was added, and the mixture was extracted twice with 100 g of toluene to give 332 g of a toluene solution containing methyl trans-3,3-dimethyl-2-(1-hydroxy-2-hydroperoxy-2-methylpropyl)cyclopropanecarboxylate and methyl trans-3,3-dimethyl-2-(2-hydroxy-1-hydroperoxy-2-methylpropylcyclopropanecarboxylate. The value of LC corrected percentage area for the total of methyl trans-3,3-dimethyl-2-(1-hydroxy-2-hydroperoxy-2-methylpropyl)cyclopropanecarboxylate and methyl trans-3,3-dimethyl-2-(2-hydroxy-1-hydroperoxy-2-methylpropylcyclopropanecarboxylate was 78%. In the toluene solution, methyl trans-3,3-dimethyl-2-(1,2-dihydroxy-2-methylpropyl)cyclopropanecarboxylate was contained at 17% (the value of LC corrected percentage area).

To 166 g of the toluene solution obtained above was added 8.3 g of dimethyl sulfide, followed by stirring at room temperature for 2 days and holding to give the reaction mixture containing methyl trans-3,3-dimethyl-2-(1,2-dihydroxy-2-methylpropyl)cyclopropanecarboxylate. The reaction mix-

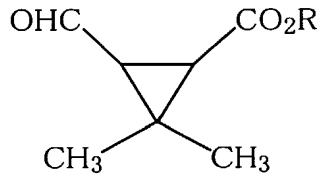
ture was concentrated under reduced pressure conditions to give about 90 g of concentrated residue. To the concentrated residue was added 39 g of toluene and then added dropwise 78 g of 15 wt.% aqueous sodium periodate solution at an internal temperature of 0°C over 10 minutes. After stirring at the same temperature for 1 hour to effect reaction, insoluble matter was removed by filtration from the reaction mixture. The resulting filtrate was subjected to phase separation to give 147 g of the organic layer containing methyl trans-3,3-dimethyl-2-formylcyclopropanecarboxylate. The GC analysis of the organic layer showed that the content for methyl trans-3,3-dimethyl-2-formylcyclopropanecarboxylate was 5.2 wt.% and the yield of methyl trans-3,3-diemthyl-2-formylcyclopropanecarboxylate on the basis of methyl trans-3,3-dimethyl-2-(2-methyl-1-propenyl)cyclopropanecarboxylate was 89%.

Industrial Applicability

According to the present invention, important aldehydes as the intermediates for the synthesis of pyrethroid-type household agents for epidemic prevention, pesticides, or the like can be produced without using highly toxic reagents or special equipment, and therefore, the process of the present invention is industrially more advantageous.

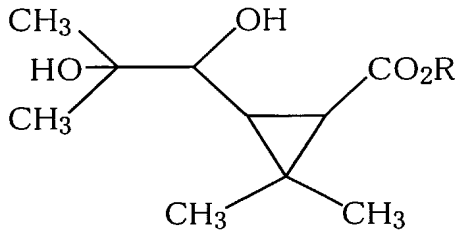
CLAIMS

1. A process for the production of an aldehyde of formula (2):



(2)

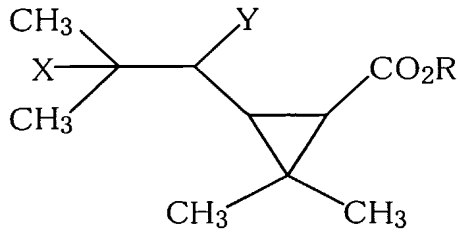
wherein R is substituted or unsubstituted alkyl, substituted or unsubstituted aryl, or substituted or unsubstituted aralkyl, which process comprises reacting a diol compound of formula (1):



(1)

wherein R is as defined above, with an oxidizing agent selected from a periodic acid compound, a hypohalogenous acid compound, a bismuth compound, or an activated manganese dioxide.

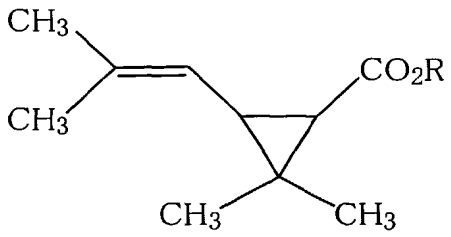
2. The process for the production of an aldehyde according to claim 1, wherein the diol compound of formula (1) is a diol compound obtained by reacting a hydroperoxy compound of formula (3):



(3)

wherein R is the same as defined in connection with formula (1), and one of X and Y is hydroxyl and the other is hydroperoxy, with a reducing agent.

3. The process for the production of an aldehyde according to claim 2, wherein the hydroperoxy compound of formula (3) is a hydroperoxy compound obtained by reacting an olefin compound of formula (4):



(4)

wherein R is the same as defined in claim 2, with hydrogen peroxide in the presence of a metal oxide catalyst obtained by reacting at least one selected from the group consisting of tungsten metal, molybdenum metal; a tungsten compound comprising tungsten and an element of Group IIIb, IVb, Vb, or VIb; and a molybdenum compound comprising molybdenum and an element of Group IIIb, IVb, Vb, or VIb, with hydrogen peroxide.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/JP 03/00954

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C67/333 C07C69/757 C07C67/31

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07C C07B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, PAJ, WPI Data, BEILSTEIN Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	page 562, paragraph 3 -page 563; figure 1	1-3

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
15 May 2003	06/06/2003

Name and mailing address of the ISA	Authorized officer
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Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/JP 03/00954

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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